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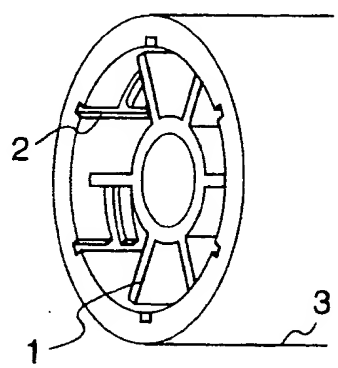
(54) HOLLOW FIBER MEMBRANE MODULE

(57) A hollow fiber membrane module comprising a module case and a hollow fiber membrane bundle comprising a plurality of hollow fiber membranes, at least one end of the bundle being bonded to and fixed on the module case, wherein the bonding portions of the hollow fiber membrane bundle and the module case comprise a silicone type resin and in at least one of the bonding portions, a reinforcing rib for reinforcing the bonding portions is directly fixed on the module case. According to the hollow fiber membrane module of this invention, the membrane filtration treatment of water containing ozone over a long period of time and the repeating washing with water containing ozone are made possible.

FIG. 1



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charging the suspended materials which have piled up between the hollow fiber membranes by routine aeration-flushing (stated as an air-bubbling). However, these membrane modules use a silicone rubber as an adhesive for bonding and fixing the membrane used on the module case, and hence, they lack strength and are inconvenient in conducting a stable filtration on a commercial scale over a long period of time though they can be applied to a short time use or to a use in a small module diameter. Therefore, a development of a more improved membrane module has been strongly desired.

Disclosure of the Invention

This invention aims at providing a hollow fiber membrane module which is little deteriorated by the strong oxidizing power possessed by ozone when a large amount of water is subjected to filtration treatment using an organic hollow fiber membrane, on which membrane the piling of materials suspended in the water is hardly caused, which membrane can be used in a stable water treatment over a long period of time, and in which membrane the adhesive for bonding and fixing the hollow fiber membrane to the module case is excellent in compressive strength.

The present inventors have made extensive research and have consequently found that the above-mentioned object can be achieved by the membrane module of this invention.

This invention relates to a hollow fiber membrane module which comprises a module case and a hollow fiber membrane bundle comprising a plurality of hollow fiber membranes, at least one end of the bundle being bonded to and fixed on the module case, wherein the bonding portions of the hollow fiber membrane bundle and the module case comprise a silicone type resin and in at least one of the bonding portions, a reinforcing rib for reinforcing the bonding portion is directly fixed on the module case.

Also, the following are mentioned as preferable modes of this invention:

(1) The reinforcing rib is fixed on the module case by at least one means selected from the group consisting of screwing, combination with a notch portion provided in the module case, fusion and welding, or the reinforcing rib is integrally molded with the module case.

(2) The cross-section of the reinforcing rib perpendicular to the longitudinal direction of the hollow fiber membrane module has a radial shape, a lattice shape or a combined shape of radial shape and concentric shape.

(3) The reinforcing rib is one flat plate or a combination of plural flat plates arranged in parallel to the longitudinal direction of the hollow fiber membrane module and has a plurality of perforated holes on said flat plate.

(4) The whole of the reinforcing rib is embedded in the bonding portion.

(5) The module case and the reinforcing rib are composed of any one of stainless steel, fluorine type resin and chlorine type resin or a combination thereof.

(6) The hollow fiber membrane is composed of a fluorine type resin.

(7) The bonding portion of the hollow fiber membrane and the module case is composed of a silicone type resin obtained by curing a liquid silicone rubber.

(8) The bonding portion of the hollow fiber membrane and the module case is a silicone type resin obtained by curing an addition type liquid silicone rubber, the viscosity before the curing is 10 mPa • sec to 250 Pa • sec, and the weight average molecular weight before the curing is in the range of from 5,000 to 300,000.

(9) The bonding portion of the hollow fiber membrane and the module case is a silicone type resin obtained by curing an addition type silicone rubber and the JIS-A hardness as measured by the measurement method of JIS K6301 after the curing is at least 30, and the tensile strength at break is at least 2 MPa.

Brief Description of the Drawings

Fig. 1 is a perspective view showing an example of the reinforcing rib and module case having notch portions of this invention.

Fig. 2 is a perspective view showing an example of the reinforcing rib and module case having notch portion of this invention.

Each of Figs. 3 to 7 is a cross-sectional view showing an example of the reinforcing rib of this invention.

Fig. 8 is a cross-sectional view showing an example of the module of this invention.

Fig. 9 is the A-A' cross-sectional view of the module of Fig. 8.

Fig. 10 is a cross-sectional view showing an example of the module of this invention.

Fig. 11 is the B-B' cross-sectional view of the module of Fig. 10.

Fig. 12 is a cross-sectional view showing an example of the module of this invention.

Fig. 13 is the C-C' cross-sectional view of the module of Fig. 12.

Fig. 14 is a cross-sectional view showing an example of the module of this invention.

Fig. 15 is the D-D' cross-sectional view of the module of Fig. 14.

materials other than the organic materials contribute greatly to the clogging, and as a result, such a fear is caused that it may constitute an obstacle to the stable filtration. Moreover, since the amount of materials passing through the membrane without being filtered is increased, a membrane having a large pore diameter affects adversely the water quality after the filtration and particularly when the filtered water is used as tap water, it becomes difficult to keep the water quality satisfactory.

From the above-mentioned matters, the hollow fiber membrane of this invention is one in the region of the microfiltration membrane in which the average pore diameter is preferably 0.01 to 1 μm, more preferably 0.1 to 0.5 μm. In this case, the average pore diameter can be measured by an air flow method (ASTM: F316-86).

The size of the hollow fiber membrane is usually such that the outer diameter is 0.5 to 5 mm and the inner diameter is 0.2 to 4.5 mm, from the viewpoint of pressure loss, membrane strength and filling efficiency.

In this invention, the hollow fiber membrane is composed of a fluorine type resin in that it can withstand the strong oxidative action of ozone. Specifically, the fluorine type resin includes polytetrafluoroethylene (PTFE), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-hexafluoropropylene-perfluoroalkyl vinyl ether copolymer (EPE), tetrafluoroethylene-ethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), chlorotrifluoroethylene-ethylene copolymer (ECTFE), polyvinylidene fluoride (PVDF) and the like. In particular, from the viewpoint of being excellent in ozone resistance and mechanical strength as a membrane, ETFE, PCTFE and PVDF are preferred, and in addition, from the viewpoint of being excellent in moldability, PVDF is more preferable.

As other materials for the hollow fiber membrane, a ceramic membrane can be mentioned from the viewpoint of ozone resistance, but the ceramic membrane is high in cost at present and is economically undesirable.

The hollow fiber membrane in this invention can be prepared by a known method. For example, a hollow fiber membrane having a three-dimensional, reticular structure can be prepared by adopting such a method as a wet method which comprises preparing a liquid mixture of the starting resins using a solvent or the like, thereafter ejecting the liquid mixture in the hollow state from a nozzle and molding the ejected mixture with a coagulating agent or the like; a method which comprises heating a mixture of the starting resins with a solvent to form a uniform solution and thereafter cooling this solution to cause phase separation; or the like. Moreover, it is also possible to prepare a hollow fiber membrane of porous membrane by a so-called stretching method, an interface pealing method, a radiation etching or the like. Furthermore, JP-A-3-215535 discloses a method of preparing a hollow fiber membrane by a mixing extraction method, and such a method can be mentioned as a preferable method. This method consists of mixing the PVDF resin with an organic liquid or inorganic powder, thereafter melt-molding the mixture, then extracting the organic liquid or inorganic powder from the resulting molded article. In this case, as the inorganic powder, hydrophobic silica is preferably used.

As a material for the module case used in the hollow fiber membrane module of this invention, there can be mentioned generally stainless steel which is excellent in ozone resistance, for example SUS-304, SUS-304L, SUS-316, SUS-316L or the like. The stainless steel has a heavy weight, so that there is such a disadvantage that the workability relating to mounting, exchange and the like of the membrane module becomes bad, or the like. However, it has an advantage that reuse is easy, and hence, it can be mentioned as a preferable material.

In view of excellent ozone resistance, light weight and good workability, the following resins can also be mentioned as materials for the module case: Fluorine type resins such as polytetrafluoroethylene (PTFE), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-hexafluoropropylene-perfluoroalkyl vinyl ether copolymer (EPE), tetrafluoroethylene-ethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), chlorotrifluoroethylene-ethylene copolymer (ECTFE), polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF) and the like; chlorine type resins such as polyvinyl chloride (PVC), polyvinylidene chloride (PVDC) and the like; etc.

In addition, from the viewpoint of mold-ability, low cost and the like, a module case in which the above-mentioned stainless steel is combined with the resin can be also used in the hollow fiber membrane module of this invention.

From the viewpoint of ozone resistance, moldability, mechanical strength and the like, the fluorine type resin to be used as the material for the module case is preferably ETFE or PVDF, more preferably PVDF, and the chlorine type resin is preferably PVC. The chlorine type resin is slightly inferior in ozone resistance to the fluorine type resin, but the module case has a thickness to a certain extent (1 mm to 10 mm) necessary for keeping its strength and the like, so that even if a slight deterioration is caused in the surface layer portion, it can be sufficiently used depending upon conditions under which the membrane is used, for example, ozone concentration, temperature and use period. PVC is generally less expensive than the expensive fluorine type resin and excellent in mechanical strength and moldability, so that it can become a preferable material for the module case of this invention. Incidentally, PVC includes rigid and soft types, and the rigid type is used in this invention.

The bonding portion of the bundle of hollow fiber membranes and the module case is required to be excellent in ozone resistance as a matter of course, and also excellent in mechanical strength after bonding, hardness, bonding strength of the bundle of hollow fiber membranes to the module case, and further excellent in processability at the time of preparation of the module. For example, when a melt-bonding method using a fluorine type resin excellent in ozone

having thixotropic properties is measured according to JIS Z8803.

The higher the cross-linking density of polymer of the liquid silicone rubber, the better the ozone resistance of the bonding portion. This cross-linking density can be controlled by varying the amount of a polyfunctional cross-linking agent added to the liquid silicone rubber.

In this invention, the adhesive can have added thereto a filler such as silica, carbon black, carbon fluoride or the like for increasing the mechanical characteristics. In this case, when the filler content is too high, the adhesiveness is deteriorated owing to a decrease of the content of the base polymer, and there is a fear of a leakage of water from the bonding portion and the like. Usually, the filler content is 5 to 80% by weight, preferably 10 to 50% by weight.

A liquid silicone rubber in which a part of the side chain of the base polymer has been fluorinated is excellent in ozone resistance and can be used as a preferable adhesive in this invention. The following formulas (2) show examples of the structural formulas thereof:

$$-\!\!\left[\begin{array}{c} CH_3 \\ | \\ \mathrm{SiO} \\ | \\ CH_2CH_2CF_3 \end{array}\right]_n\!\!-\ ,\quad -\!\!\left[\begin{array}{c} CH_3 \\ | \\ \mathrm{SiO} \\ | \\ CH_3 \end{array}\right]_m\!\!-\ \text{and/or}\ -\!\!\left[\begin{array}{c} CH_3 \\ | \\ \mathrm{SiO} \\ | \\ CH{=}CH_2 \end{array}\right]_l\!\!-$$

In the above formulas, each of n, m and l is the number of the repeating unit determined by the molecular weight of the base polymer mentioned above.

When the silicone resin to be used in the bonding portion is selected, in view of the mechanical strength and durability required to the hollow fiber membrane of this invention, the characteristics thereof after the curing are such that the JIS-A hardness as measured by the measurement method of JIS K6301 is at least 30, preferably at least 40, and more preferably at least 50, and the strength at break is at least 2 MPa, preferably at least 5 MPa and more preferably at least 6 MPa.

In this invention, specific examples of the adhesive include, for example, TSE322, TSE322B, TSE3221, TSE3212, TSE3253, TSE326, TSE3331, TSE3337, TSE3033, TSE3320 and TSE3315 manufactured by Toshiba Silicone Co., Ltd.; FE61, KE1202, KE1206, KE1216, KE1602, KE106, KE109, KE109E, KE1204 and KE1302 manufactured by Shin-Etsu Silicone Co., Ltd.; SE1711, SE1750, SE1701 and CY52-237 manufactured by Toray • Dow Corning • Silicone Co., Ltd.; and the like. In particular, TSE322, TSE3337, FE61 and the like are preferred because the original mechanical properties thereof are high and the deterioration of physical properties thereof due to ozone is small.

However, even when a silicone rubber having a relatively high strength as mentioned above is used, a large size module employed in industrial uses causes cohesive failure in the bonding portion and cannot withstand long term use in some cases though it depends upon the thickness of the bonding portion. Such a case can be met by making the thickness of the bonding portion so large as not to cause cohesive failure; however, as compared with an adhesive which is usually used, for example, an epoxy resin, a urethane resin or the like, the silicone rubber is very expensive, and when the amount of the silicone rubber used is increased, the production cost is elevated sharply and the number of sites which do not contribute to filtration in the longitudinal direction of the hollow fiber membrane becomes large, the amount of water obtained per membrane module becomes low, and the running cost is increased. Therefore, such a meeting method cannot be said to be desirable.

On the other hand, the present inventors have found that by providing a reinforcing rib fixed directly on the inner wall of the module case in the bonding portion of the hollow fiber membrane and the module case, the cohesive failure in the bonding portion can be prevented. According to this method, the amount of the silicone rubber used can be decreased and, in addition, the fixing of the reinforcing rib on the module case can be conducted, for example, by fixing by screwing into the inner wall of the module case, by fixing by a combination with the notch portion provided in the module case, by fusion-fixing, by weld-fixing or by molding integrally with the module case. According to such a fixing method, the reinforcing rib can be easily processed and a cost suitable to industrial uses can be obtained. Here, the fusion means melting to bond the materials of both module case and reinforcing rib together with an ultrasonic wave, heat or solvent in the state that the reinforcing rib has been inserted into the module case. Also, the weld means fixing the module case and the reinforcing rib by heat using a welding rod or the like in the state that the reinforcing rib has been inserted into the module case.

The method of receiving the hollow fiber membrane bundle into the module case includes a method which comprises fixing the reinforcing rib on the module case and thereafter receiving the hollow fiber membrane bundle into the module case and a method which comprises placing the hollow fiber membrane bundle up on at least one reinforcing

the diameter of the hollow fiber membrane bundle becomes large, so that a pressure loss takes place in the direction of diameter of the membrane bundle and it becomes impossible for the whole of fiber bundle to uniformly contribute to the filtration, and the amount of water filtered decreases with the lapse of time. In particular, in a module by which ozone is added to the raw water and the amount of water filtered has been sharply increased, the above influence is great. Also, even when an aeration-flushing treatment is effected for discharging the suspended materials piled on the hollow fiber membrane bundle, the conventional module structure has a low effect on the removal of suspended materials accumulated in the 180°-opposite direction to the nozzle and in the central portion of fiber bundle, and particularly when raw water having ozone added thereto is filtered, inorganic suspended materials are much attached to the membrane, so that it is necessary that the module have such a module structure that the aeration-flushing effect is high. The aeration-flushing referred to herein means such an operation as to strip off the suspended materials piled on the membrane surface and/or the suspended materials accumulated between the hollow fiber membranes by aeration and further discharge the piled materials and/or the accumulated materials by flushing out of the system, namely, out of the module or apparatus. Aeration and flushing may be effected successively or simultaneously.

The sectional shape of the opening provided in the bonding portion includes circle-shape, ellipse-shape, fan-shape, triangle-shape, tetragon-shape, hexagon-shape, slit-shape and the like. In particular, one having a circle-shaped or ellipse-shaped section is preferred because the liquid-contacting surface area per sectional area of opening becomes minimum and the pressure loss of the fluid becomes small.

Moreover, when the number of openings provided in the bonding portion is greater, the accumulation of the suspended materials in the module is hardly caused, while the number of fillable hollow fiber membranes filled in the module becomes small, and the amount of water permeated becomes small as much. The number of openings is varied depending upon the diameter of module and the shape of opening and, for example, when the module has a 3-inch diameter the number of openings is 3 to 30. When the module has a 5-inch diameter the number of openings is about 4 to 80.

The opening area percentage of the openings provided in the bonding portion is expressed by the following numerical formula (3), and it is 10 to 40%, preferably 15 to 35%:

$$K = \frac{S \times N}{R^2 \times \pi \times M} \times 100 \qquad (3)$$

wherein K is the opening area percentage, S is the sectional area of one opening, N is the number of openings, R is the outer radius of the hollow fiber membrane and M is the number of hollow fiber membranes.

As the system of gathering filtered water, there can be used either a one end water gathering system or a both ends water gathering system. In the case of the one end water gathering system, as shown in Figs. 8 to 13, one end of the hollow fiber membrane 4 is bonded in the state that the hollow fiber has been opened, and the other end is sealed with an adhesive. The opening for feeding raw water and/or a gas is provided in the bonding portion 5' in which the hollow fiber membrane is sealed with an adhesive. In the case of the both ends water gathering system, as shown in Figs. 14 and 15, the hollow fiber membrane is bonded in the state that both ends have been opened, the lower end of the module has a water-gathering chamber 11 for filtered water and a skirt-shaped cover 12 surrounding the same, and a water-gathering tube 13 is provided for taking out the filtered water in the water-gathering chamber 11 to the upper end. The opening 6 provided in the lower end bonding portion is communicated with the gap between the skirt-shaped cover 12 and the module case 3 through the perforated hole on the side of the module case.

The openings 6 provided in the bonding portions 5 and 5' of this invention are preferably provided in the interior of the hollow fiber membrane bundle, whereby raw water and/or a gas fed to the module spreads uniformly over the whole of the hollow fiber membranes, and it becomes difficult for the suspended materials to pile up in the gap between the hollow fiber membranes and a stable amount of water filtered is obtained over a long period of time. When this opening is provided in the outside of the hollow fiber membrane, the raw water and/or gas fed to the module tends to cause a channeling, and as a result, there is a fear that such problems may be caused that the accumulation of the suspended materials becomes easy to cause in the interior of the hollow fiber membrane bundle, the effective membrane surface area is reduced and the amount of water permeated is decreased.

Furthermore, the openings 6 provided in the bonding portions 5 and 5' are preferably so provided that the end faces of the openings are positioned on the same face as the interface of the bonding portion in the inside of the module. The accumulation of the suspended materials in the vicinity of the interface of the bonding portion of the hollow fiber membrane is thereby inhibited and a stable amount of water filtered can be obtained over a long period of time. When this opening end face projects from the interface of the bonding portion into the inside of the module, the flow is easy to stay in the lower portion than the opening end face and the entering of the gas becomes difficult, so that the accumulation of the suspended materials in the interior of the hollow fiber membrane bundle becomes easy to cause, and as a result, there is a fear that such problems may be caused that the effective membrane area is decreased and the amount of

an elongation at break of 280%.

Subsequently, an inside screw processing was applied to the one end portion of a module case made of a stainless steel having an outer diameter of 140 mm and a length of 1,100 mm. Moreover, an outside screw processing was applied to the side surface of a reinforcing rib made of a stainless steel as shown in Fig. 3, and the reinforcing rib was fixed by screwing on the above module case.

Each of the above six hollow fiber membrane bundles was received into each of the 6 spaces separated by the reinforcing rib in the module case, bonding jigs were attached to both side ends and the hollow fiber membrane was bonded to and fixed on the module case on which the reinforcing rib was fixed, with an addition type silicone rubber (TSE322 manufactured by Toshiba Silicone Co., Ltd.). Furthermore, in the side end portion on which no reinforcing rib was set up, 19 tubings made of a high density polyethylene having an outer diameter of 10 mm and a length of 55 mm were arranged so that they were uniformly distributed in the hollow fiber membrane bundle, and then bonded.

After the silicone bonded portion had been sufficiently cured, the hollow fiber membrane bundles were cut for opening the hollow portion on the side on which the reinforcing ribs were set up (the filtered water-gathering side) and for removing the 19 tubings from the other side. By removing the 19 tubings, 19 openings for feeding a raw water were formed in the bonding portion to complete the preparation of a hollow fiber membrane module of this invention as shown in Fig. 8. In this case, the reinforcing rib did not project from the bonding portion end and was completely embedded therein.

The hollow fiber membrane module prepared as mentioned above was treated with ethanol to be made hydrophilic and thereafter the ethanol in the membrane was replaced with pure water.

The hollow fiber membrane module after the replacement with water was connected to an evaluator, and a raw water-feeding nozzle and a circulation-concentrated water-discharging nozzle were connected to the piping of the apparatus, and in the state that the filtered water-gathering nozzle was not fitted with a pipe joint, filtration under pressure was conducted with pure water having a water temperature of 26°C at a feeding pressure of 500 kPa. The state of deformation of the bonding portion was checked by a strain gauge to find an about 1-mm blister at the center of each of the 6 sites separated by the reinforcing rib. In the vicinity of the portion in which the reinforcing rib was embedded, no blister was observed.

Subsequently, piping was connected to the filtered water-gathering nozzle and filtration and back wash were repeated 30,000 times using river water having a turbidity of 3 to 12 as raw water at a feeding pressure of 300 kPa at a back wash pressure of 450 kPa. In this case, an ozone gas was added to the raw water so that the ozone concentration in the filtered water became 0.3 ppm and further aeration-flushing was conducted every 1,000 cycles. After completion of the above repeating test, the bonding portion was observed to find that no deformation of the bonding portion was caused, and no crack of the bonding portion was observed. In addition, by a gastight test, leakage was checked but no leak from the bonding portion was observed. Incidentally, the gastight test was conducted by a method which comprises immersing the module in water, applying an air pressure of 1/2 of the bubble point of the membrane and checking a leak of air from the bonding portion.

Example 2 (this invention)

As a hollow fiber membrane, there were prepared four bundles each prepared by bundling 400 PVDF membranes prepared by the method disclosed in JP-A-3-215535, said PVDF membrane having an outer diameter of 1.3 mm, an inner diameter of 0.7 mm, a volume porosity of 68%, a ratio between the average pore diameter of the outer surface and the average pore diameter of the cross-section both determined from the average pore diameters of outer surface, inner surface and cross-section calculated by an electron photomicrograph of 1.75, a ratio between the average pore diameter of the inner surface and the average pore diameter of the cross-section both determined in the same manner as above of 0.85, an average pore diameter of 0.25 µm as measured by an air flow method, the maximum pore diameter of 0.35 µm as measured by a bubble point method, a ratio between the maximum pore diameter and the average pore diameter of 1.4, a water-permeation rate of 2,400 liters/m^2 · hour · 100 kPa (25°C), a strength at break of 17 MPa and an elongation at break of 240%.

Subsequently, a PVDF reinforcing rib as shown in Fig. 5 was set up in the one end portion of a module case made of a PVDF having an outer diameter of 89 mm and a length of 1,100 mm and weld-fixed thereon.

Each of the above four hollow fiber membrane bundles was received into each of the four spaces separated by the reinforcing rib in the module case, bonding jigs were attached to both side ends, and the hollow fiber membrane was bonded to and fixed on the module case on which the reinforcing rib was fixed, with an addition type silicone rubber (TSE3337 manufactured by Toshiba Silicone Co. Ltd.). Furthermore, as a bonding jig attached to the side end portion on which no reinforcing rib was set up, there was used an aluminum disk fitted at 5 places with aluminum columns having an outer diameter of 10 mm and a length of 45 mm, the surface of which was coated with a Teflon.

After the silicone bonded portion had been sufficiently cured, on the side on which the reinforcing rib was set up (the filtered water-gathering side), the hollow portion was cut to form openings and, on the other side, the bonding jig

a feeding pressure of 500 kPa in the state that the filtered water-gathering nozzle was not fitted with a pipe joint. By a strain gauge, the state of deformation of the bonding portion was checked to find that about 6-mm blister was observed in the center portion.

Subsequently, a pipe was connected to the filtered water-gathering nozzle and filtration and back wash were repeated 30,000 times using river water having a turbidity of 3 to 12 as raw water at a feeding pressure of 300 kPa at a back wash pressure of 450 kPa. In this case, an ozone gas was added to the raw water so that the ozone concentration in the filtered water became 0.3 ppm, and further aeration-flushing was conducted every 1,000 cycles. After completion of the above repeating test, the bonding portion was observed to find that in the center portion of the bonding portion, cohesive failure was caused in the state that a part containing the hollow fiber membrane bundle rose. In addition, it was confirmed that from the failure portion, three cracks started in the bonding portion.

Example 5 (Comparison)

Under the same conditions as in Example 2, except that the module case was not fitted with a reinforcing rib, a hollow fiber membrane module was prepared.

The above hollow fiber membrane module was treated with ethanol to be made hydrophilic, and the ethanol in the membrane was replaced with pure water.

After the replacement with water, the lower part of the tank was fitted with a raw water-feeding pipe and the upper part of the side surface of the tank was fitted with a concentrated water-discharging tube, and in the state that the filtered water-gathering side was not fitted with a piping, filtration under pressure was conducted with pure water having a water temperature of 25°C at a feeding pressure of 500 kPa. By a strain gauge, the state of deformation of the bonding portion was checked to observe about 3-mm blister in the center portion.

Subsequently, piping was connected to the filtered water gathering nozzle and filtration and back wash were repeated 40,000 times using river water having a turbidity of 3 to 12 as raw water at a feeding pressure of 300 kPa at a back wash pressure of 450 kPa. In this case, an ozone gas was added to the raw water so that the ozone concentration in the filtered water became 0.3 ppm, and further aeration-flushing was conducted every 1,000 cycles. After completion of the above repeating test, the bonding portion was observed to find that a part of the bonding portion (about half of the total periphery) was gone from the module case.

Example 6 (Comparison)

Under the same conditions as in Example 3, except that the module case was not fitted with a reinforcing rib, a hollow fiber membrane module was prepared.

After the above hollow fiber membrane module was treated with ethanol to be made hydrophilic, the ethanol in the membrane was replaced with pure water.

After the replacement with water, the hollow fiber membrane module was set in an evaluator, and filtration and back wash were repeated 30,000 times by an internal pressure system using river water having a turbidity of 1 to 3 as raw water at feeding pressure of 300 kPa at a back wash pressure of 500 kPa. In this case, an ozone gas was added to the raw water so that the ozone concentration in the filtered water became 0.4 ppm.

After completion of the above repeating test, the module was removed from the evaluator, and the bonding portion was observed to find that cohesive failure was caused over 2/3 periphery in the peripheral portion of the bonding portion (the portion about 10 mm distant from the wall surface of the module case).

Industrial Applicability

The hollow fiber membrane module of this invention makes possible the membrane filtration treatment of water containing ozone over a long period of time and the repeating washing (including back wash) with water containing ozone, so that its effect given the water-treating field using ozone, particularly the water works field and the like is very great.

Claims

1. A hollow fiber membrane module comprising a module case and a hollow fiber membrane bundle comprising a plurality of hollow fiber membranes, at least one end of the bundle being bonded to and fixed on the module case, wherein the bonding portions of the hollow fiber membrane bundle and the module case comprise a silicone type resin and in at least one of the bonding portions, a reinforcing rib for reinforcing the bonding portions is directly fixed on the module case.

FIG. 1

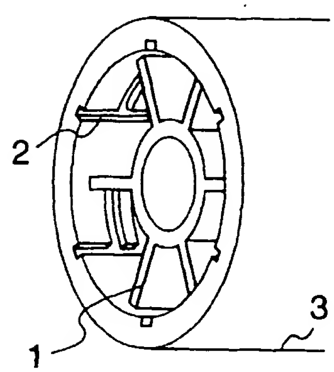


FIG. 2

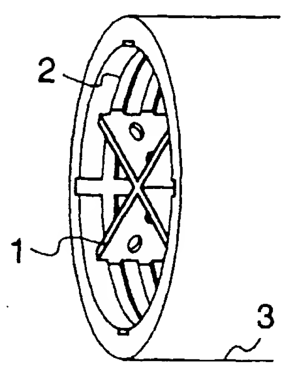


FIG. 3

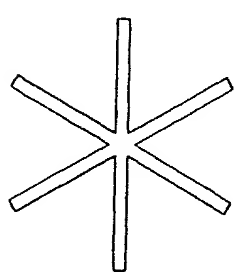


FIG. 8

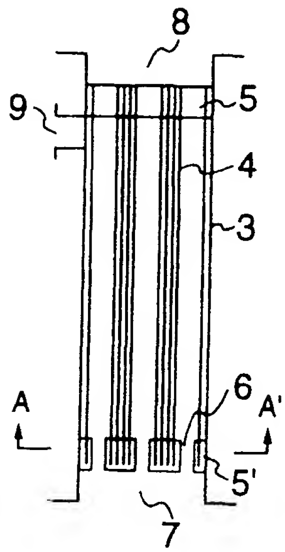


FIG. 10

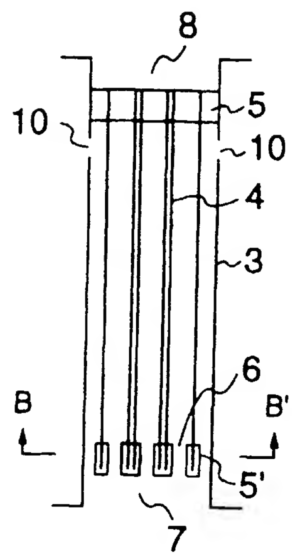


FIG. 9

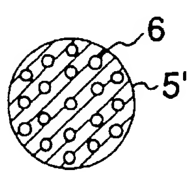


FIG. 11

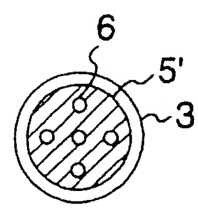


FIG. 16

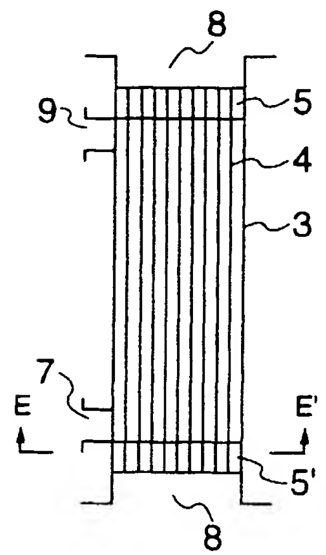
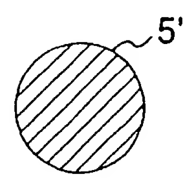


FIG. 17



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/02699

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Claim; page 3, upper left column, line 13 to upper right column, line 11; Fig. 1 (Family: none)	
A	JP, 50-73882, A (Teijin Ltd.), June 18, 1975 (18. 06. 75), Claim; page 2, upper right column, line 14 to page 3, upper left column, line 12; Figs. 1 to 2 (Family: none)	1 - 5
A	JP, 60-110390, A (Kuraray Co., Ltd.), June 15, 1985 (15. 06. 85), Page 2, lower right column, line 20 to page 3, upper left column, line 7; page 3, lower right column, lines 4 to 11 (Family: none)	6 - 7
A	JP, 61-157309, A (Daicel Chemical Industries, Ltd.), July 17, 1986 (17. 07. 86), Page 2, lower right column, line 15 to page 3, upper left column, line 9 (Family: none)	8 - 10
A	JP, 58-53202, U (Kuraray Co., Ltd.), April 11, 1983 (11. 04. 83), Claim (Family: none)	8 - 10
A	JP, 63-171607, A (Sumitomo Electric Industries, Ltd.), July 15, 1988 (15. 07. 88), Claim; page 3, lower left column, line 7 to lower right column, line 20 (Family: none)	7- 10
A	JP, 63-171606, A (Sumitomo Electric Industries, Ltd.), July 15, 1988 (15. 07.88), Claim; page 4, upper left column, line 9 to lower left column, line 1 (Family: none)	7 - 10

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